Name: SID:

Discussion Section:

FINAL EXAM
Biophysical Chemistry
Chemistry 130A
Fall 1999

Problem	Points
1	/32
2	/16
3	/26
4	/20
5	/32
6	/14
7	/20
8	/30
9	/24
Total	/214

Optional Release Form:

I , _____, authorize my grade on the final and course grade to be posted on the course website identifying me by my SID.

_____   _____

          Sign Here   Date

Show all your work

State your assumptions and check that they hold

Many problems have multiple parts. Usually, latter parts are
Independent of earlier parts! So DON'T give up!

Circle Numerical Answers!

Physical Constants

Gas Constant	R	=	8.3145 J/K mol	**Boltzmann constant**	k	=	$1.381*10^{-23}$ J/K
		=	0.08205 L atm/K mol				
RT @ 25ºC	RT	=	2.479 kJ/mol	**kT @ 25ºC**	kT	=	$4.116*10^{-21}$ J
		=	24.464 L atm/mol				
Faraday constant	F	=	$9.648*10^4$ C/mol	**K_f for H_2O @ 1 atm**	K_f	=	1.86 K kg solvent/moles solute
	1atm	=	$1.01325*10^5$ Pa	= 760 Torr	=		760 mmHg

Physical Equations

Raoult's Law	$P_A = X_A P_A^{\circ}$	Henry's Law	$P_B = k_B X_B$
van't Hoff Eq.	$\ln\dfrac{K_2}{K_1} = -\dfrac{\Delta H^{\circ}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$	Osmotic Pressure	$\ln(a_A) = \dfrac{-\pi\overline{V}_A}{RT}$
Freezing/Boiling Changes	$\left|\Delta T_{f,b}\right| = K_{f,b} m_B$	Osmotic Pressure	$\pi = cRT$
Freezing/Boiling Changes	$\left|\Delta T_{f,b}\right| = \dfrac{M_A RT_o^2}{1000\Delta H_{fus,vap}} m_B$	Free Energy	$\Delta G = \Delta G^{\circ} + RT\ln(Q)$
Chemical Potential	$\mu = \mu^{\circ} + RT\ln(a)$	Free Energy	$dG = VdP - SdT + \mu dn + \gamma dA + ZFd\phi + Mgdh - M\omega^2 dx$
Total Energy	$\Delta E = q + w$	Enthalpy	$\Delta H = \Delta E + \Delta(PV)$
Heat Capacity	$q = \displaystyle\int_{T_1}^{T_2} CdT$	Entropy	$dS = \dfrac{dq_{rev}}{T}$
Average Translational Energy	$\langle U_{tr}\rangle = \dfrac{3}{2}kT$	Mean Speed	$<u> = \left(\dfrac{8kT}{\pi m}\right)^{1/2}$
Maxwell Distribution	$P(u) = 4\pi\left(\dfrac{m}{2\pi kT}\right)^{3/2} u^2 e^{-mu^2/2kT}$	Mean Square Speed	$<u^2> = \dfrac{3kT}{m}$
Boltzmann Distribution	$\dfrac{P_j}{P_i} = \dfrac{N_j}{N_i} = \dfrac{g_j}{g_i} e^{-(E_j-E_i)/kT}$	collisions per second per molecule	$z = \sqrt{2}\pi\dfrac{N}{V}\sigma^2\langle u\rangle$
Mean Free Path	$\lambda = \dfrac{<u>}{z}$	collisions per unit volume per unit time	$Z = \left(\dfrac{N}{V}\right)\dfrac{z}{2}$
Scatchard Equation	$\dfrac{v/N}{[A]} = K(1 - v/N)$	Hill Equation	$\dfrac{f}{1-f} = K[A]^n$
Fick's 1st Law	$J_x = -D\dfrac{dc}{dx}$	Michaelis-Menten Law	$v = k_{cat} E_{tot}\dfrac{[S]}{K_M + [S]}$
Pressure	P=ρgh	Diffusion Constant	$D = <x^2>/2t$
Arrhenius' Law	$k = A\exp(\dfrac{-E_a}{RT})$	Transition State Theory	$k = \dfrac{k_B T}{h}\exp(\dfrac{\Delta S^{\ddagger}}{R})\exp(\dfrac{-\Delta H^{\ddagger}}{RT})$
Nernst Equation	$\varepsilon = \varepsilon^0 - \dfrac{RT}{nF}\ln(Q)$		

1. (32 pts)

    a. **(6 pts)** State the four laws of thermodynamics as precisely and mathematically as possible. Remember to consider both system and surroundings. We'll do the last one for you.

        Zeroth Law:

        First Law:

        Second Law:

        Third Law: A perfect crystal at 0 K has zero entropy. S(perfect crystal, 0 K)= 0

b. **(11 pts)** How many arrangements are possible for 2 balls in 5 cells if only one ball can occupy a cell at one time and if:

    i.   The balls are indistinguishable?

    ii.   If there is one red ball and one blue ball?

    iii.   Which case has the higher entropy? Why?

Name: SID:

c. **(15 pts)** Assume that a perfect crystal has states A and B that are separated by an energy ΔE and are the only states. A is lower in energy than B. A and B are populated according to the Boltzmann distribution.
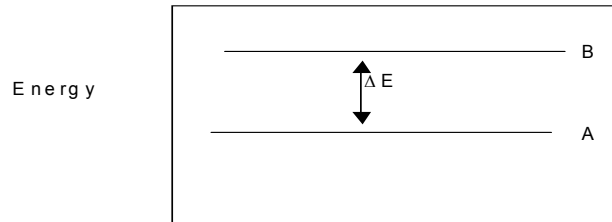
i.   Show that only state A is occupied at 0 K. (Hint: show $\dfrac{P(E_B)}{P(E_A)} = 0$.)

ii.   Can State B ever be more probable than State A?

iii.   How does (i) relate to the Third Law of Thermodynamics?

2. **(16 pts)** You are 300 meters under water. In the problem assume blood is water.

   a) **(10 pts)**What is the mole fraction of N_2 in your blood if the Henry's Law constant for N_2 in water is 8600 atm at body temperature?

                           o   78% by volume of the the air in your SCUBA gear is N_2

                           o ρ_{Hg}= 13.6 g/ml, ρ_{H20}= 1.00 g/ml

                           o   Assume blood is an ideal solution.

b) **(6 pts)** The average adult has 3.20 liters of blood. If you suddenly return to the surface, what volume of N_2 bubbles out of your blood at 1.00 atm and 20.0 °C? (The molecular weight of water is 18.02 g/mol.)

3. **(26 pts)** Suppose that when a particular channel in the sarcoplasmic reticulum (SR) in a cell is activated it allows calcium ion to flow across the SR membrane. In fact, it is found that this particular channel transports four ions at a time into the cell cytoplasm. In this particular cell the potential of the cytoplasmic side is 100 mV less than inside the SR. Consider the system at 37 °C. It is measured that there is 20.0 μM Ca^{2+} in the SR of the cell and 1.00 μM Ca^{2+} in the cytoplasm.

(a) (18 pts).

    i. **(12 pts)** In the absence of active transport, what is the value of the free energy per mole for the transport of calcium from the SR to the cytoplasm of the cell? In which direction will the calcium ion spontaneously flow through the membrane channel?

    ii. **(6pts)** Given that $\Delta G°$ for the hydrolysis of ATP is -31.3 kJ/mol and that the reaction quotient, Q, for the hydrolysis is about 10^{-2} determine the minimum amount of ATP which would need to be hydrolyzed in order to reverse the spontaneous direction of the calcium flux found in part i.

(b) (4 pts) Assume that a single channel in the SR is activated and in a very short space of time has transported a small amount of calcium from the SR to the cytoplasm and then has closed. This leaves a small point source of calcium ion just at the SR membrane. The tiny sphere contains w_0= 40 nanograms of Ca^{2+}. The diffusion constant for calcium ion in cytoplasm is $64*10^{-6}$ cm^2/sec. The number of grams per ml of calcium ion at a distance r away from the sphere at any time is:

$$c(r,t) = \frac{w_o}{(4\pi Dt)^{3/2}} \exp(-\frac{r^2}{4Dt})$$

Suppose there is a receptor 20 micrometers (microns) away from the tiny sphere. It requires at least 8 $\mu g/cm^3$ of ion locally around the receptor in order to be activated. Will it be activated at t=10 milliseconds after the channel opening? Ignore any blocking of calcium diffusion by cellular structures.

(c) (4 pts) In real cells there are hundreds of proteins in the cytoplasm that bind calcium ion. What would you expect, qualitatively, would be the effect of these proteins on the apparent diffusion constant for Ca^{2+} and its peak concentration at any point?
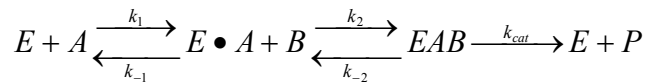
4. (20 pts) Consider an enzyme that takes two substrates to a final product

$$A+B+E \rightarrow E + P$$
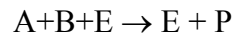
The reaction can occur one of two ways: 1) It might be an ***ordered*** reaction mechanism in which A binds to E first and then B binds to the EA complex, or 2) it might be a ***random*** reaction mechanism in which either A or B can bind the enzyme first followed by subsequent binding of the other species.

a) **(8 pts)** The reaction diagram for the ***ordered*** binding reaction may be written as:

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E \bullet A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EAB \xrightarrow{k_{cat}} E + P$$

Draw a similar style diagram for the ***random*** binding mechanism.

b) **(12 pts)** Solve for the rate of product formation for the **ordered** binding reaction in terms of total enzyme and free substrate concentrations using the rapid equilibrium approximation for the first two reversible steps. Use $K_A = \dfrac{[E][A]}{[EA]}$ and $K_B = \dfrac{[EA][B]}{[EAB]}$.

5. (32 pts) When liquid water in a completely filled, closed container is placed in a special freezer (deep-freeze) at -20 °C, the pressure in the container increases up to P_{final} atm at equilibrium. ΔH_{fus} for water is 333.4 kJ/kg; the density of liquid water is 1.00g/cm^3 and the density of water ice is 0.9172 g/cm^3.

a. **(8 pts)** Find the ΔG_{fus} of water at -20°C, 1.00 atm. Be sure to state any assumptions you make!

b. **(6 pts)** What is the volume change per kg of water when it goes through the liquid to solid phase change?

c. **(8 pts)** Calculate the change in ΔG_{fus} due to a pressure increase from 1.00 atm to P_{final} at constant temperature, in terms of P_{final}. State any assumptions.
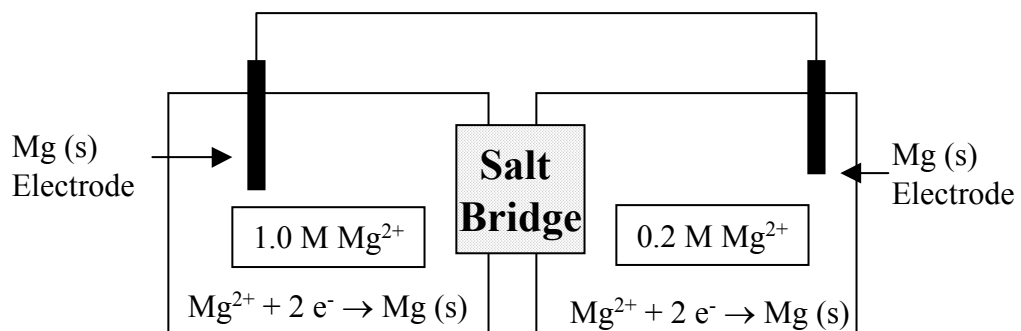
d. **(10 pts)** Find P_{final}.

6. (14 pts) There are two *Non-ideal* solutions in an electrochemical cell as follows:

Mg (s) Electrode

Salt Bridge

1.0 M Mg^{2+}

$Mg^{2+} + 2\ e^- \rightarrow Mg\ (s)$

0.2 M Mg^{2+}
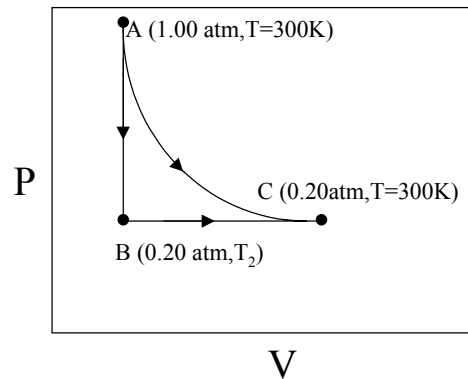
$Mg^{2+} + 2\ e^- \rightarrow Mg\ (s)$

Mg (s) Electrode

Find the electrical potential of the cell at 25 °C. Assume the activity coefficients are approximately constant over this concentration range.

7. (20 pts) This question concerns the following processes for 1.00 mole of an ideal gas:

Where Path I goes A→B→C and Path II goes from A→C and

Process A→B is constant volume, irreversible depressurization.

Process B→C is constant pressure, irreversible expansion.

Process A→C is an isothermal, reversible expansion

a. **(9 pts)** Calculate the difference in work following Path I versus Path II for 1 mole of an ideal gas.

b. **(7 pts)** Calculate ΔS for Path I and for Path II.

c. **(4 pts)** Qualitatively, compare the efficiency of one cycle of A→C→B→A to that of one cycle of a Carnot engine.

8. (30 pts) Consider the gas phase dissociation of cyclobutane (abbreviated Cy) into ethylene (abbreviated Eth): $Cy \rightarrow 2$ Eth. One proposed mechanism for the process is:

$$Cy + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cy^* + M$$

$$Cy^* \xrightarrow{k_2} 2Eth$$
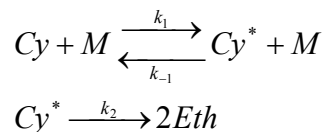
where M is some molecule present in the system which collides with Cy in order to give it enough energy to dissociate (Cy^* is energized Cy).

a) **(10 pts)** Make the steady-state approximation for $[Cy^*]$ and show that the rate of appearance of ethylene is

$$\frac{1}{2}\frac{d[Eth]}{dt} = k_{tot}[Cy] \quad , \text{ where } k_{tot} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$$

b) **(8 pts)** Show that for very small [M], the rate is 2nd order overall, and that for very large [M], the rate is first order overall. Sketch k_{tot} as a function of [M].

c) **(12 pts)** Suppose that you model k_{tot} as an Arrhenius-theory rate constant, and measure an activation energy of 3.50 kJ/mol. What is the ratio of the rate constant at 298 K to that at 273 K? Assuming $\Delta H^{\ddagger} \approx E_a$ and $\Delta S^{\ddagger} \approx$ constant over this temperature range, what is the ratio of rates at the two temperatures if you assume a transition state theory form for k_{tot}? If the error in your experimental rates is +/- 10% can you tell the difference between the two theories in this case? *Note that there are three questions here!*

9. (24 pts) For a system with different chemical species, A,B, C present, the Gibbs free energy is generalized to dG= VdP-SdT+$\mu_A$dn$_A$+$\mu_B$dn$_B$+$\mu_C$dn$_C$ where n$_A$ is the number of moles of species A, etc. In this problem we'll consider the equilibrium A+B⇔C

a) **(10 pts)** Show that if we have equilibrium at a constant T and P, μ_A+μ_B=μ_C. (Hint: At equilibrium, $\dfrac{\partial G}{\partial n_a}=0$ and dn$_A$,dn$_B$ and dn$_C$ are related to each other.)
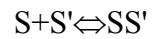
b) **(8 pts)** Given that μ_A+μ_B=μ_C show that the equilibrium constant is:

$$K_{eq} = \exp\left(\frac{\mu_A^\circ + \mu_B^\circ - \mu_C^\circ}{RT}\right)$$

c) **(6 pts)** Consider the association reaction of 2 complementary strands of DNA at 310K.

$$S+S' \Leftrightarrow SS'$$

Suppose that the equilibrium concentrations are [S]=[S']=1.50 nM and that [SS']= 9.00 nM, and that the activity coefficients of the three species are 0.750. If we want $\Delta G°$ within 5% of the exact answer, can we assume an ideal solution?